

Determination of Lead in Unleaded Gasoline on the Liberty Series II ICP-OES with the Axially-Viewed Plasma

Application Note

Inductively Coupled Plasma-Optical Emission Spectrometers

Author

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Introduction

In the past twenty-five years, the determination of lead in unleaded petrol has become important as various studies have shown that most of the lead released into the environment is from the combustion of gasoline. In 1986, the United States Environment Protection Agency (USEPA) reported that 90% of the total lead released into the environment in the United States was the result of lead emission from gasoline combustion [1].

With the introduction of unleaded gasoline, the need to measure even lower levels of lead has become necessary.

Due to the widely held belief that ICP-OES with axial-viewing exacerbates problems with molecular band emissions and carbon build-up when analyzing organic liquids, it is not often considered for the analysis of organic liquids [2], particularly highly volatile organic liquids such as gasoline. Recent advances in ICP-OES technology have overcome these problems, so that the axially-viewed ICP can be used with confidence for the analysis of organic liquids.

This work describes the determination of lead in unleaded gasoline by ICP-OES with axially-viewed plasma, oxygen accessory and volatile organics kit, to overcome the effects of the gasoline matrix.

The extremely high vapor pressure of gasoline overloads the plasma which destabilizes, or may even extinguish, the plasma. Plasma flicker adversely affects the stability of the signal. A cooled spray chamber reduces the solvent load into the plasma and results in a much more stable signal.

The Auxiliary Gas Module 1 (AGM-1) oxygen accessory adds a small flow of oxygen to the argon auxiliary gas to reduce molecular band emissions and carbon build-up in the torch injector tube and on the Cooled Cone Interface of the Liberty axially-viewed Series II spectrometer.

This work also shows that in the analysis of gasoline, lower detection limits are attainable for lead using the axially-viewed plasma compared to the radially-viewed



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plasma [3]. The accuracy of the method has been assessed by the use of National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 2712 Pb in Reference Fuel, which contains tetraethyl lead.

Experimental

Instrumental

An Agilent Liberty Series II ICP-OES with the axially-viewed plasma, AGM-1 oxygen accessory and cooled glass spray chamber were used.

The Liberty Series II ICP features a 40 MHz, free running RF generator, a 0.75 m Czerny-Turner monochromator with a 1800 grooves/mm holographic grating used in up to four orders. The resolution of the optical system ranges from 0.018 nm in 1st order to 0.006 nm in 4th order.

The instrument was controlled with a Digital Equipment Corporation (DEC) Celebris computer with an Intel Pentium processor and Agilent's Plasma 96 software running under Microsoft Windows 95 operating system.

The instrument operating conditions are listed in Table 1.

Table 1. Instrument Operating Conditions

| | |
|---------------------------|---|
| Power | 1.5 kW |
| Plasma gas flow | 16.5 L/min |
| Auxiliary gas flow | 1.5 L/min |
| Spray chamber type | Cooled glass spray chamber |
| Spray chamber temperature | -10 °C |
| Torch | Demountable torch with an 0.8 mm id injector tube |
| Nebulizer | Standard glass concentric nebulizer |
| Nebulizer pressure | 90 kPa |
| AGM-1 setting | 210 mL/min |
| Pump tube | Inlet – Viton, orange-orange, 0.89mm id Outlet – Viton, grey-grey, 1.30 mm id |
| Pump speed | 10 rpm |
| Sample uptake rate | 0.5 mL/min |
| Integration time | 5 seconds |
| Fast pump | Off |
| Grating order | Pb 261.418 nm - 2nd order Pb 283.306 nm - 2nd order |
| Background correction | Offpeak Pb 261.418 nm - left 0.010 nm, right 0.010 nm Pb 283.306 nm - left 0.010 nm, right 0.010 nm |
| PMT voltage | 650 V |

Reagents

- Analytical reagent grade organic solvents and chemicals were used
- Iso-octane, (Unichrom, Ajax chemicals)
- Toluene, (BDH)
- Dekalin (decahydronaphthalene), (Unilab, Ajax Chemicals)
- Aliquot 336 (tricaprylmethylammonium chloride), (Aldrich Chemicals)
- Iodine, (Univar, Ajax Chemicals)
- 10% v/v Aliquot 336/dekalin solution: dissolve 5 mL (or 4.4 g) of Aliquot 336 into 50 mL
- 3% w/v iodine solution: dissolve 1.5 g of iodine crystals in toluene and dilute to 50 mL

Premium unleaded gasoline was obtained from a service station.

Dekalin was used as the rinse solution.

Standard Preparation

A 10 mg/L Pb secondary standard was prepared by accurately weighing 2 g of a 500 mg/kg Conostan S21 standard in hydrocarbon oil and diluting to 100 mL in iso-octane.

Working standards were then prepared by pipetting 1.25 mL and 2.50 mL of the 10 mg/L Pb standard solution into 25 mL volumetric flasks [3]. Then 20.00 mL of the unleaded gasoline sample was added to each flask, followed immediately by the addition of 0.3 mL of 3% iodine solution.

This was mixed well and allowed to stand for 5 minutes. Then 0.5 mL of the 10% Aliquot 336/dekalin solution was added. It was made up to volume with dekalin and mixed well. The final solutions contained 0.5 mg/L and 1.0 mg/L Pb additions, respectively.

Sample Preparation

20.00 mL of the unleaded gasoline sample was transferred to a 25 mL volumetric flask followed immediately by the addition of 0.3 mL of 3% iodine solution.

This was mixed well and allowed to stand for 5 minutes. Then 0.5 mL of the 10% Aliquot 336/dekalin solution was added and made up to volume with dekalin and mixed well.

For the NIST SRM 2712 Pb in Reference Fuel, 3.00 mL of the sample was transferred to a 25 mL volumetric flask. Then 20.00 mL of the unleaded gasoline was added followed imme-

diately by 0.3 mL of 3% iodine solution. This was mixed well and allowed to stand for 5 minutes. Then 0.5 mL of the 10% Aliquot 336/dekalin solution was added and made up to volume with dekalin and mixed well.

Iodine is added to form iodo lead alkyl anions which are then stabilized by the addition of a quaternary ammonium salt such as aliquot 336. This treatment ensures that all alkyl lead compounds (tetramethyl lead and tetraethyl lead) in the sample and organometallic lead in the standard give identical response.

Results and Discussion

The standard additions calibration method was used for the determination of lead in unleaded gasoline.

The 261.418 nm and 283.306 nm lead lines were selected for the analysis based upon detection limits and freedom from spectral interference. The more intense 220.353 nm lead line was not used due to spectral interference from the matrix at this wavelength. Care must be taken when using the standard additions calibration method as the presence of spectral interferences, such as from the matrix, will still produce a linear calibration but the determined concentration will be higher than the true value.

The mean results of four analyses are listed in Table 2.

Table 2. Results of the Analysis

| Sample | Pb measured value at 261.418 nm (mg/L) | Pb measured value at 283.306 nm (mg/L) | Pb certified value (mg/L) |
|-------------------|--|--|---------------------------|
| Unleaded gasoline | 0.507 ± 0.004 | 0.525 ± 0.003 | — |
| NIST SRM 2712 | 7.7 ± 0.2 | 7.8 ± 0.1 | 7.9 ± 0.3 |

The measured values of the standard reference material for the 261.418 nm and 283.306 nm lead lines compare well with the certified value. Similar results were also obtained for both lines for the unleaded gasoline sample confirming the accuracy of the method.

The measured values of the unleaded gasoline sample are well within the specified limits for the lead content in unleaded gasoline.

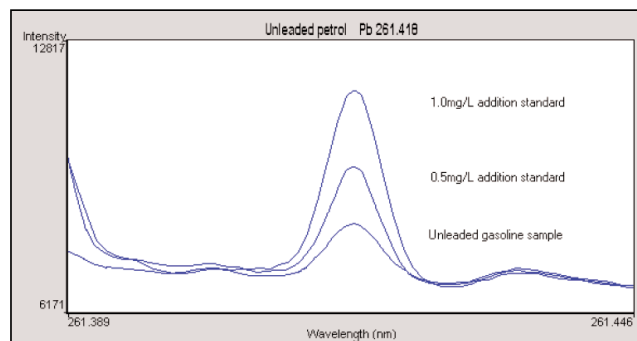


Figure 1. Wavelength scans of addition standards 1 and 2 and the unleaded gasoline sample at the Pb 261.418 nm line.

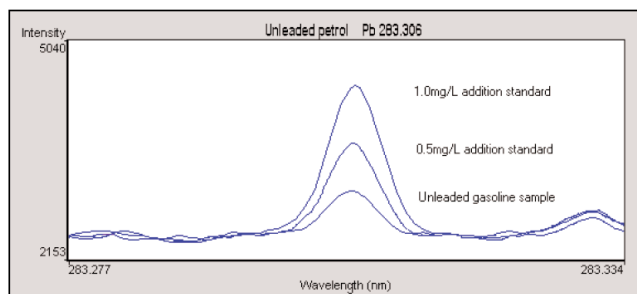


Figure 2. Wavelength scans of addition standards 1 and 2 and the unleaded gasoline sample at the Pb 283.306 nm line.

Long Term Stability

Long term stability was evaluated by performing a calibration and then analyzing the unleaded gasoline sample that had been spiked with 1 mg/L of Pb, Cu, Ti and Zn. The reproducibility of the measurements over one hour ranged from 0.9 to 1.1 %RSD. The long term stability plots are displayed in Figure 3.

Five replicates were measured at an integration time of three seconds for each line. The precision for each measurement ranged from 0.2 to 1.1 %RSD

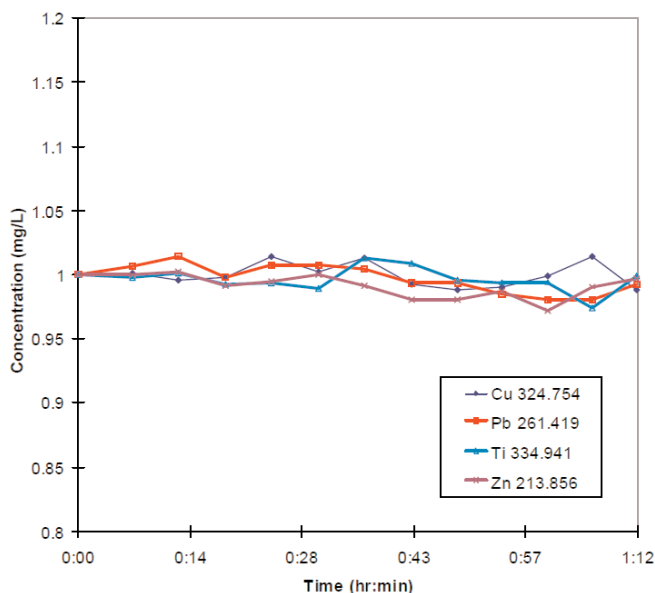


Figure 3. Signal stability over one hour for 1 mg/L of Cu, Pb, Ti and Zn spiked in unleaded gasoline.

Detection Limits in Iso-octane

The detection limit (3 sigma) of lead in iso-octane was determined for the 261.418 nm and 283.306 nm lines using an integration time of 5 seconds and 10 replicates. These are compared with those determined on the ICP-OES with the radially-viewed plasma [3].

The results are listed in Table 3.

Table 3. Detection Limits in Iso-octane

| Element | Wavelength nm | Axial ICP detection limit µg/L | Radial ICP detection limit µg/L |
|---------|---------------|--------------------------------|---------------------------------|
| Pb | 261.418 | 11 | 50 |
| Pb | 283.306 | 12 | 75 |

It has also been observed for the analysis of organic solvents on the axially-viewed ICP that using a higher plasma gas flow allows more oxygen to be injected into the plasma. With more oxygen present in the plasma, lower background and therefore improved signal to background ratios and detection limits are observed.

Summary

The determination of lead in unleaded gasoline on the Liberty Series II with axially-viewed plasma using the AGM-1 oxygen accessory and volatile organics kit has been described. An improvement in detection limits of a factor of about 5 to 6 fold compared with the radially-viewed plasma have been observed for the 261.418 nm and 283.306 nm lead lines.

The measured value of lead in NIST SRM 2712 is in good agreement with the certified value and long term stability and short term precision are excellent.

References

1. "Air quality criteria for lead". USEPA, EPA-600/8-83/028, I-IV, US EPA, Triangle Park, North Carolina, **1986**.
2. D. R. Demers "Evaluation of the Axially-viewed (End-on) Inductively Coupled Argon Plasma Source for Atomic Emission Spectroscopy", Applied Spectroscopy, **1979**, 33, 584-591.
3. T. Nham "Determination of lead in unleaded gasoline by ICP-AES with the use of oxygen and a cooled spray chamber", Varian Australia Pty. Ltd., Mulgrave, Victoria 3170, Australia, ICP-AES At Work no. 15, October **1993**.

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Printed in the USA
November 1, 2010
ICPES-22



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